

AMENDED SPECIFICATION

Reprinted as amended in accordance with the Decision of the Principal Examiner acting for the Comptroller General dated the twenty second day of February, 1974, under Section 14, of the Patents Act, 1949.

PATENT SPECIFICATION

1302 221

1302221

NO DRAWINGS

(21) Application No. 15623/70 (22) Filed 2 April 1970

(31) Convention Application No. P 19 17 278.2

(32) Filed 3 April 1969 in

(33) Germany (DT)

(44) Complete Specification published 4 Jan. 1973

(51) International Classification C09B 29/36

(5.2) Index at acceptance

C4P 1A3 1C 1D3 1F1 1F2

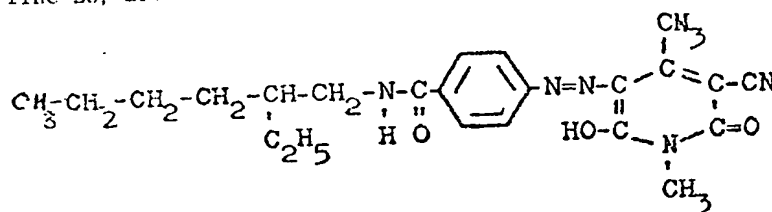


PATENTS ACT 1949

AMENDED SPECIFICATION NO 1302221

The following amendments were allowed under Section 29 on 6 January 1976

Page 16, line 26, *delete* formula *insert*



THE PATENT OFFICE
2 February 1976

Bas 26865/14

PATENTS ACT 1949

AMENDED SPECIFICATION NO 1302221

SLIP NO 2

The following corrections were allowed under Section 76 on 3 July 1975

Page 1, line 1, (71) after We, insert BASF AKTIENGESELLSCHAFT, formerly known as,

THE PATENT OFFICE
5 March 1976

Bas 27587/1/2

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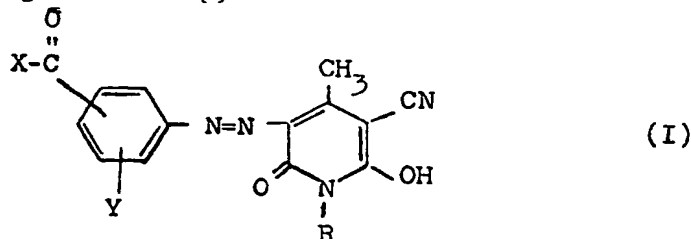
(19)



(54) NEW MONOAZO DYES OF THE PYNDONE SERIES

(71) We, BADISCHE ANILIN- & SODA-FABRIK AKTIENGESELLSCHAFT, a German Joint Stock Company, of 6700 Ludwigshafen, Federal Republic of Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to new azo dyes and their production. The new dyes have the general formula (I):

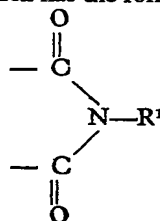


wherein, for X and Y, either

X denotes hexyloxy, ethylhexyloxy, benzyloxy, phenoxy, β - hydroxypropoxy, γ -hydroxypropoxy, ω -hydroxybutoxy, ω -hydroxyhexoxy,
 $-(OCH_2CH_2)_2OCH_3$, $-(OCH_2CH_2)_2OC_2H_5$, $-(OCH_2CH_2)_3OCH_3$,
 $-(OCH_2CH_2)_3OC_2H_5$, $-OCH_2CH_2OCOCH_3$,
 or a radical of the formula $-NHR^8$, where R^8 denotes an alkyl radical having 4 to 8 carbon atoms and optionally substituted by hydroxy or by alkoxy having 1 to 4 carbon atoms, a methoxypropyl or ethoxypropyl radical or a 5-membered to 8-membered cycloalkyl radical, and

Y denotes hydrogen, chlorine, bromine, nitro, cyano or a radical having the formula $-COX$, or

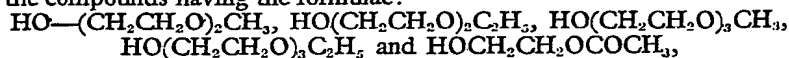
Y together with the radical $-COX$ denotes a radical which is attached to adjacent carbon atoms of the benzene ring and which has the formula



R^1 denoting hydrogen, alkyl which has 1 to 8 carbon atoms and is optionally hydroxy-, methoxy- or ethoxy-substituted, phenyl or tolyl; and

R denotes alkyl having one to four carbon atoms, alkyl having two to four carbon atoms and substituted by hydroxy, by dimethylamino or by alkoxy of one to four carbon atoms, benzyl, phenylethyl, phenyl, tolyl, 2-methoxyphenyl, 3-methoxyphenyl, 4-methoxyphenyl, 2-chlorophenyl, 3-chlorophenyl, 4-chlorophenyl, 2-hydroxyphenyl, 3-hydroxyphenyl or 4-hydroxyphenyl.

Alkoxy-carbonyl radicals COX as substituents for the diazo components may thus contain any of the following alcohol components: hexanol, ethylhexanol, benzyl alcohol, phenol, the compounds having the formulae:



and the compounds β -hydroxypropanol, γ -hydroxypropanol, 1,4-di-hydroxybutane and 1,6-dihydroxyhexane.

The following are examples of radicals of the formula $-\text{NHR}^1$ for X: N-butyl-amino, N-cyclohexylamino, N-(β -ethylhexyl)-amino, N- β -hydroxyethylamino, N- β -methoxyethylamino, N- β -hydroxypropylamino, N- γ -hydroxypropylamino, N- γ -methoxypropylamino, and N- γ -ethoxypropylamino.

The following aniline derivatives are given as examples of diazo components: the β -ethylhexyl, benzyl, phenyl, methyl diglycol, ethyl diglycol, methyl triglycol, ethyl triglycol, β -acetoxyethyl, γ -hydroxypropyl, 4-hydroxybutyl or 6-hydroxyhexyl esters of 2-aminobenzoic, 3-aminobenzoic and 4-aminobenzoic acids, the methyl diglycol ester of 4-nitroanthranilic acid, the di(methyl diglycol), di(ethyl diglycol) and dibenzyl esters of 3-aminophthalic, 4-aminophthalic, 5-aminoisophthalic and aminoterephthalic acids.

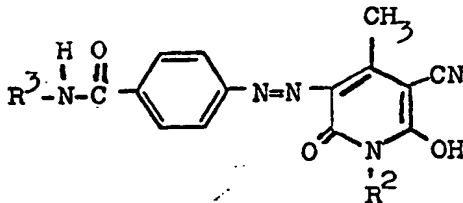
The following may also be referred to as suitable diazo components: the n-butyl-amides, isobutylamides, cyclohexylamides, methoxypropylamides, ethoxypropylamides, β -hydroxyethylamides and anilides of 3-amino benzoic acid and 4-aminobenzoic acid, the di(methoxypropylamide) or di(n-butylamide) of 5-aminoisophthalic acid, and the imides, β -hydroxyethylimides, γ -hydroxypropylimides, methylimides, n-butylimides, -methoxypropylimides or phenylimides of 3-aminophthalic acid and 4-aminophthalic acid.

Industrially preferred dyes are obtained with diazo components which have been derived from anilines having a monosubstituted amide group, CONHR^2 in which the amide group is substituted by an alkyl radical having 4 to 8 carbon atoms and optionally substituted by hydroxy or by alkoxy having 1 to 4 carbon atoms, a methoxypropyl or ethoxypropyl radical or a 5-membered to 8-membered cycloalkyl radical. The compounds in which R^2 contains four or more carbon atoms have a higher affinity for polyester fibres than those in which R^2 contains less than four carbon atoms. Those in which R^2 bears a hydroxy or alkoxy-substituent are also of particular value.

Examples of radicals R in the dyes having the general formula are: methyl, ethyl, propyl, n-butyl, isobutyl, β -methoxyethyl, γ -methoxypropyl, β -hydroxyethyl, β -hydroxypropyl, γ -hydroxypropyl, γ -ethoxypropyl, γ -dimethoxypropyl, benzyl, phenylethyl, phenyl, tolyl, 2-methoxyphenyl, 3-methoxyphenyl, 4-methoxyphenyl, 2-chlorophenyl, 3-chlorophenyl, 4-chlorophenyl, 2-hydroxyphenyl, 3-hydroxyphenyl or 4-hydroxyphenyl.

Preferred radicals R are the methyl group and alkyl groups having two to four carbon atoms which may bear hydroxy or alkoxy groups having one to four carbon atoms, particularly methoxy and ethoxy, as substituents.

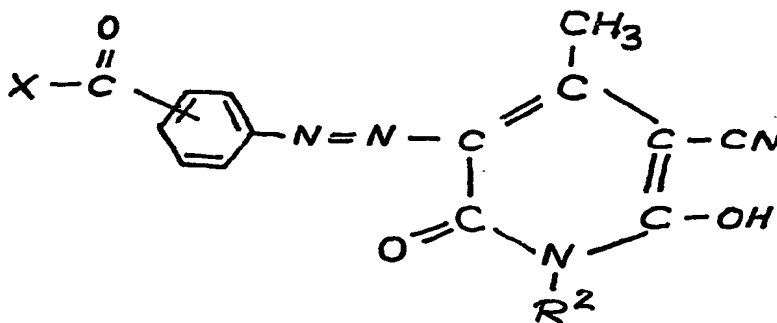
One group of preferred dyes which has particular technical significance is comprised of the compounds having the formula:



where R^2 denotes an alkyl radical having one to four carbon atoms, or an ethyl or propyl radical bearing a hydroxy, methoxy, propoxy, ethoxy or butoxy group as substituent; and R^3 denotes an alkyl radical having four to eight carbon atoms, e.g. butyl or β -ethylhexyl, and optionally bearing hydroxy or alkoxy having one to four carbon atoms as substituents, a methoxypropyl or ethoxypropyl radical, a five-membered to

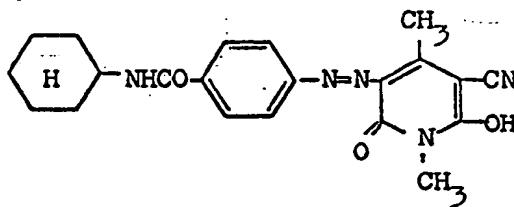
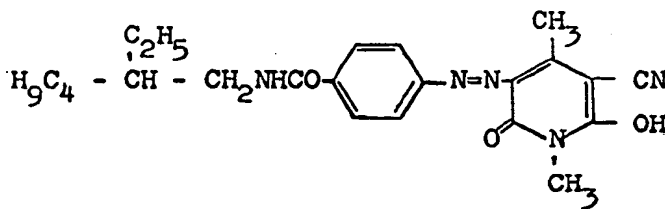
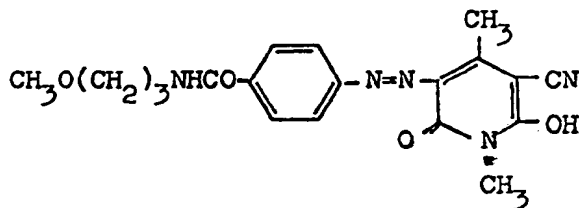
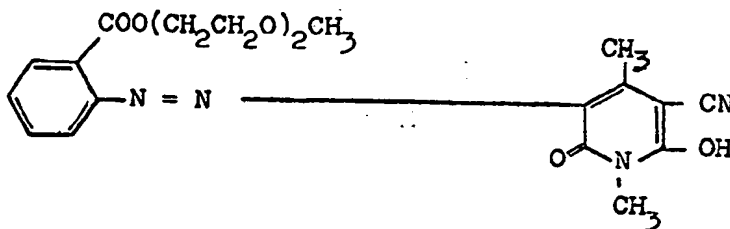
eight-membered cycloalkyl radical, e.g. cyclohexyl, or a γ - or β -hydroxypropyl, β -hydroxyethyl, β -methoxyethyl or β -ethoxyethyl radical.

Another class of preferred dyes is composed of compounds of the formula:



in which R^2 is as defined above, preferably alkyl of 1 to 4 carbon atoms or γ -methoxypropyl, and X is $-(OCH_2CH_2)_nOZ$, Z being ethyl or, preferably, methyl and n being 2 or 3. Dye of this class also give particularly advantageous results in the dyeing of polyester fibres.

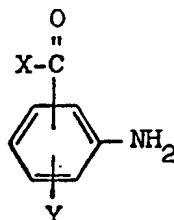
Examples of preferred dyes are the following.



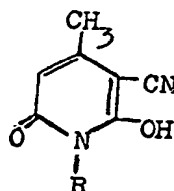
The new dyes are yellow and give greenish yellow to orange dyeings having excellent fastness properties on synthetic fibrous material such as polyamides, polyacrylonitrile and particularly on cellulose esters and polyesters. The fastness to light and dry-heat pleating and setting are particularly good. For the production of the new dyes, diazo compounds of amines having the general formula

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may be reacted with coupling components having the general formula :



R, X and Y being as defined above.

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Coupling may be carried out as usual in an aqueous medium, with or without the addition of solvents, at a weekly acid to alkaline pH.

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The invention is illustrated by the following Examples. References to parts and percentages in the following Examples relate to weight unless otherwise stated.

EXAMPLE 1.

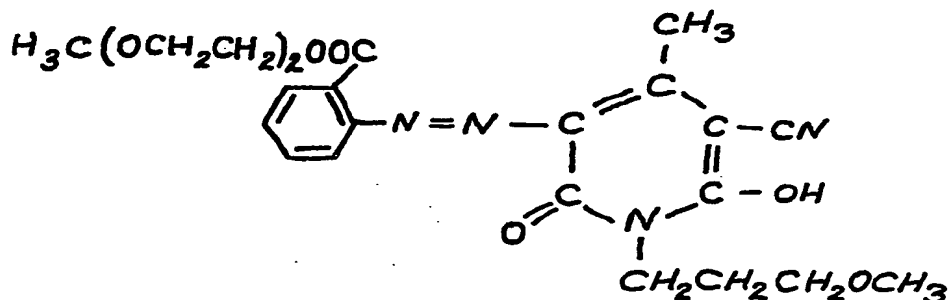
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160 parts of ice is added to a solution of 23.9 parts of the methyldiglycol ester of 2-aminobenzoic acid in 160 parts of water and 25 parts by volume of concentrated hydrochloric acid and then 30 parts by volume of 23% sodium nitrite solution is allowed to flow in at 0° to 5°C. The whole is stirred at the same temperature for another two hours and any excess of nitrous acid present is then removed as usual. The diazo solution is added in portions to a solution of 22.9 parts of N-γ-methoxypropyl-2-hydroxy-3-cyano-4-methylpyridone(6), 5 parts of sodium hydroxide and 10 parts of sodium carbonate in 300 parts by volume of water with an addition of 200 parts of ice. When coupling is over, the deposited dye having the formula:

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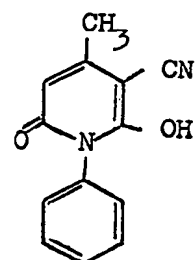
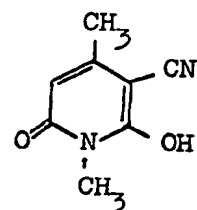
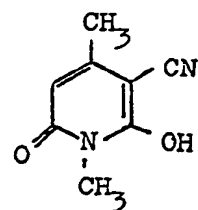
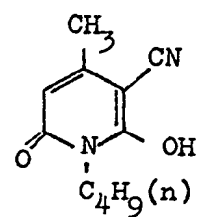
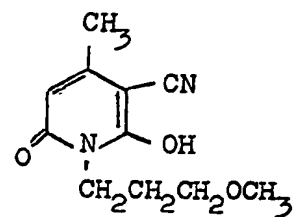
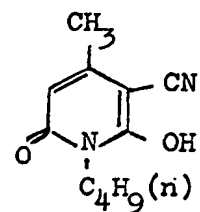
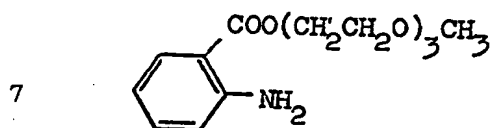
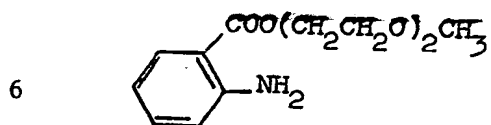
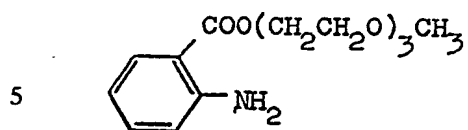
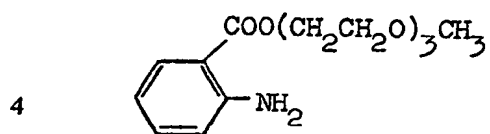
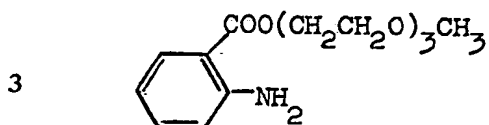
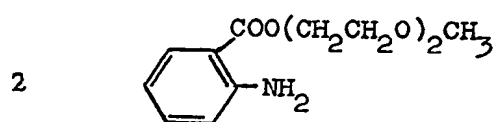


is suction filtered, washed with water and dried. It is obtained in the form of a yellow powder which dissolves in dimethylformamide with a yellow color.

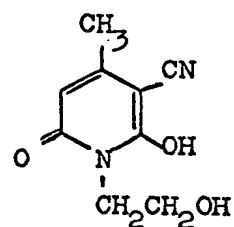
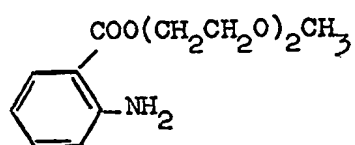
100 parts of polyethylene terephthalate cloth is dyed in a dye liquor containing 1 part of the finely divided dye thus obtained, 2 parts of the sulfonated adduct of 80 moles of ethylene oxide to 1 mole of sperm oil alcohol and 2,000 parts of water for sixty minutes at 120°C in a pressure apparatus. A pure greenish yellow dyeing is obtained which has good thermal resistance and outstanding fastness to light.

Using the diazo components and coupling components set out in the following Table, dyes having similar tinctorial properties are obtained by analogous methods.

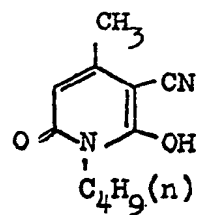
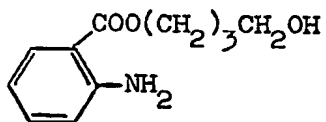
In the following Examples 2 to 48, the dyeings on polyester in Examples 24, 25, 28, 29 and 32 are yellow and those in all the other Examples are greenish yellow.



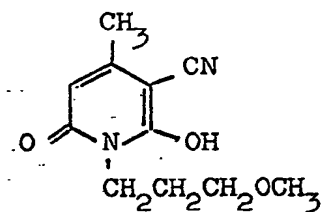
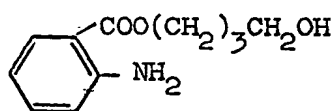
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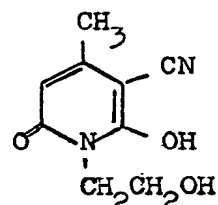
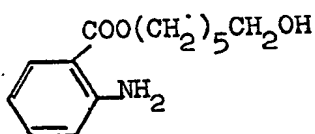
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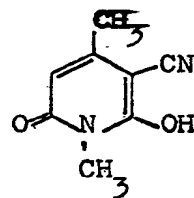


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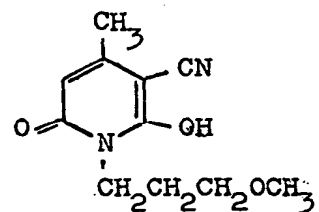
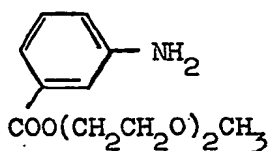


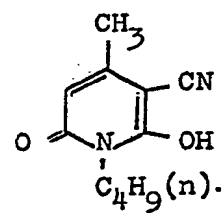
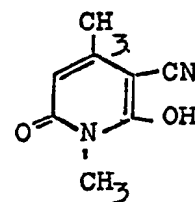
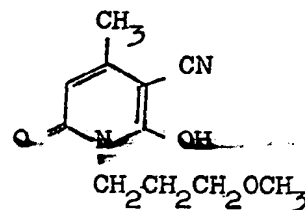
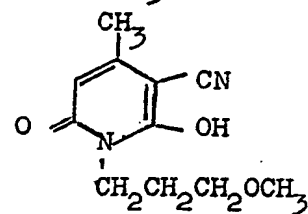
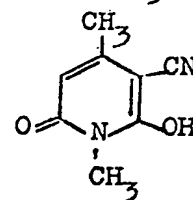
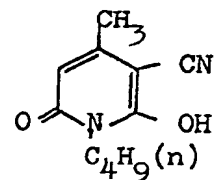
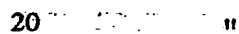
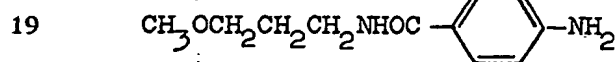
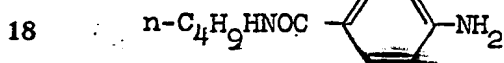
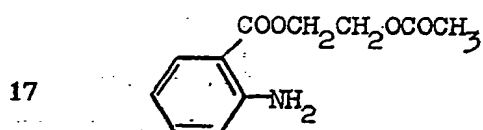
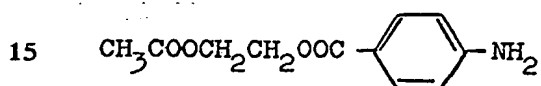
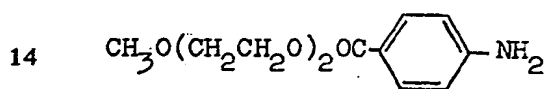
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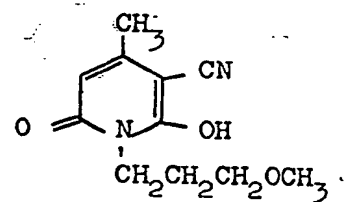
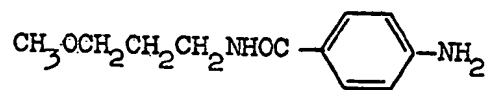


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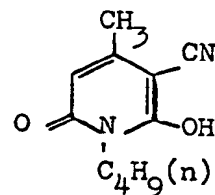
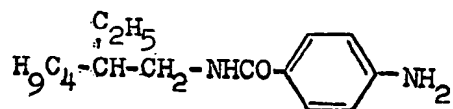




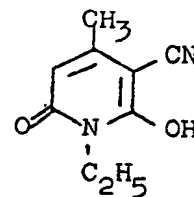
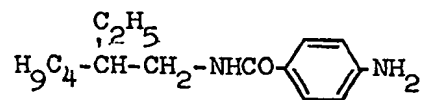
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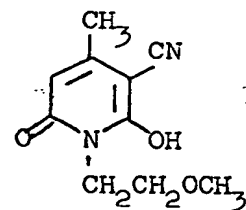


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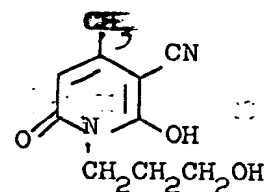
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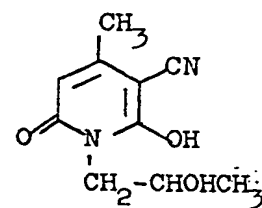
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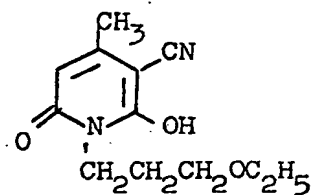
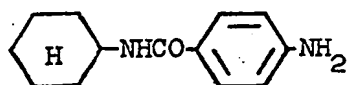


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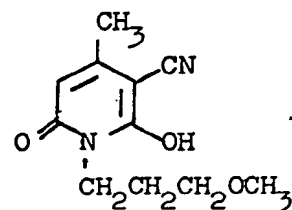


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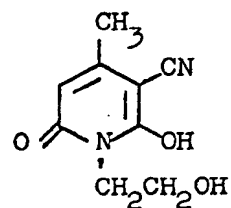
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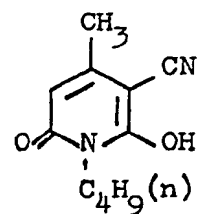
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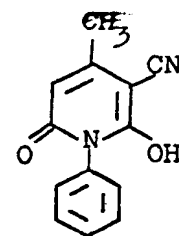
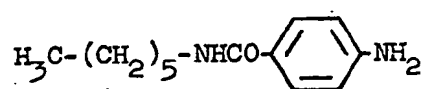


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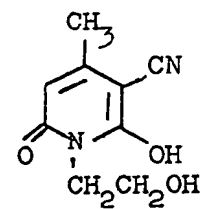


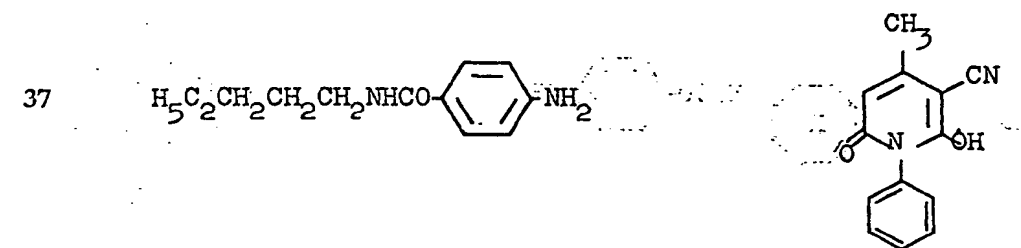
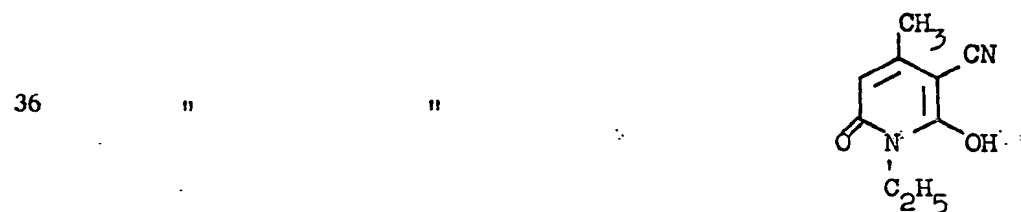
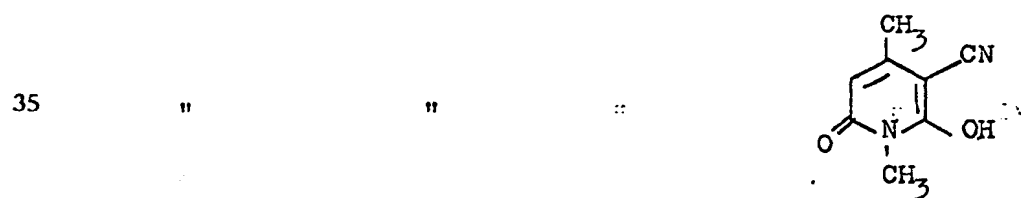
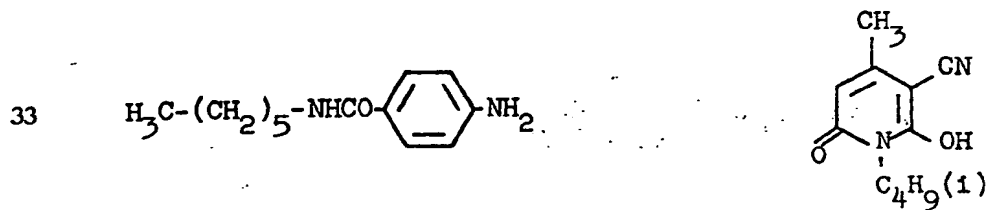
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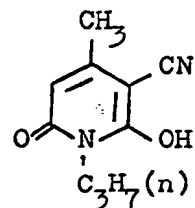
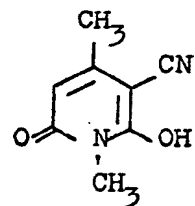
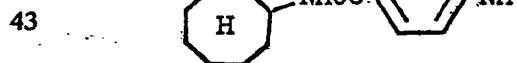
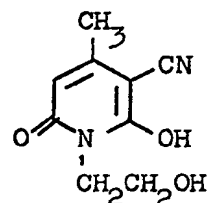
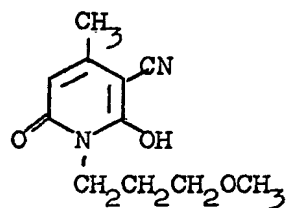
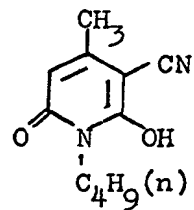
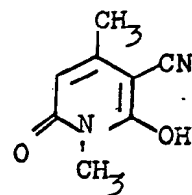
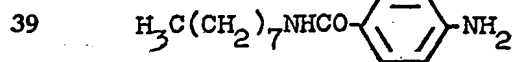


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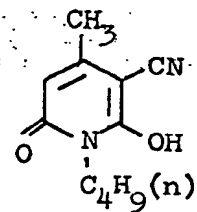
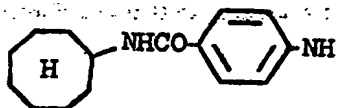
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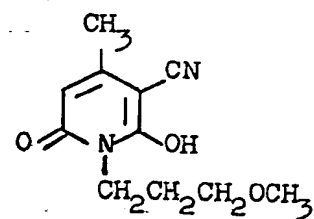


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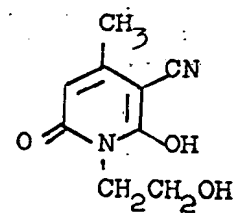
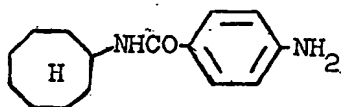


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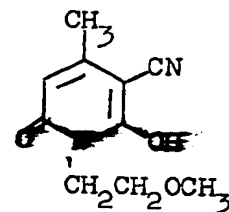


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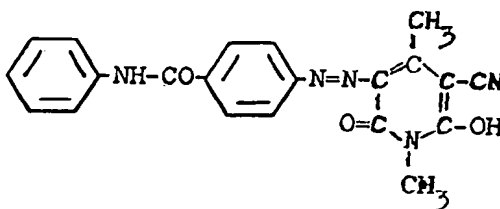
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EXAMPLE 49.

21.2 parts of p-aminobenzanilide is stirred at room temperature for several hours with 300 parts by volume of water and 0.3 part of the reaction product of oleylamine with about 12 moles of ethylene oxide. 25 parts by volume of concentrated hydrochloric acid and 300 parts of ice are added and then 30 parts by volume of 23% sodium nitrite solution is allowed to flow in slowly at 0°C to 5°C. The whole is stirred for another two hours and any excess of nitrous acid present is removed by adding sulfamic acid. Coupling onto a 22.9 parts of N-methyl-2-hydroxy-3-cyano-4-methyl-pyridone-(6) is carried out by a method analogous to that described in Example 1. A yellow dye is obtained having the formula:



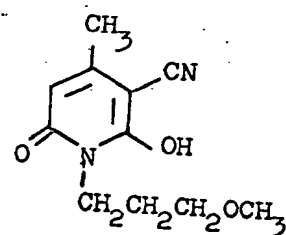
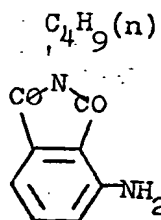
which dissolves in dimethylformamide giving a brown color and dyes polyethylene terephthalate cloth orange shades having excellent fastness properties.

Dyes having similar fastness properties are obtained by an analogous method with the diazo components and coupling components set out in the following Table. The shade of the dyeing on polyesters is greenish yellow in Example 50 and yellow in Examples 51 to 54.

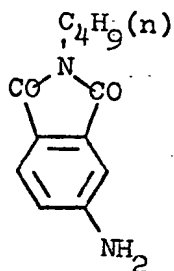
Example Diazo component

Coupling component

50

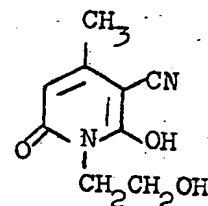
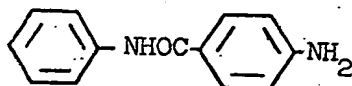


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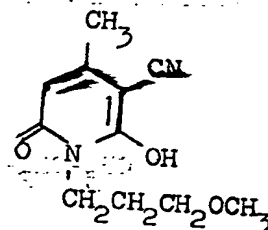
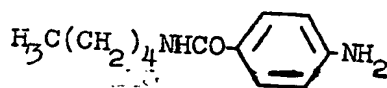


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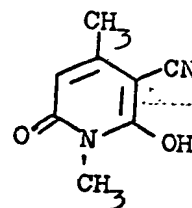
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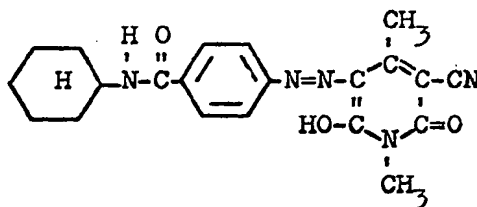
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EXAMPLE 55.

109 parts of p-aminobenzoic cyclohexylamide is stirred with 2000 parts of water and 140 parts of concentrated hydrochloric acid. Two hours later 500 parts of ice is added. 156 parts of 23% sodium nitrite solution is then added to the suspension at 0° to 5°C in the course of thirty minutes. The whole is stirred for two hours and the solution is allowed to flow through a filter within thirty minutes into a solution of 84 parts of 1,4-dimethyl-2-hydroxy-3-cyano-pyridone-(6) in 1500 parts of water and 42 parts of 50% caustic soda solution. 45 parts of sodium carbonate and 1000 parts of ice are then added. The temperature should be 4° to 8°C during coupling; the pH is from 7 to 8. The whole is stirred overnight and the dye is suction filtered and washed with 2000 parts of water.

200 parts of the dye having the formula:

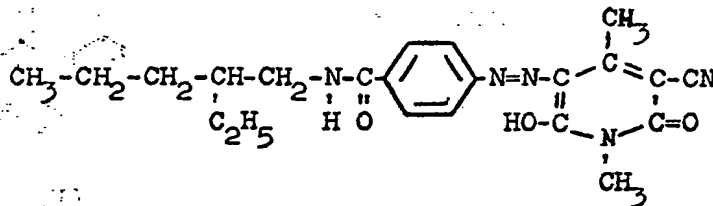


is obtained.

EXAMPLE 56.

124 parts of p-aminobenzoic isooctylamide is stirred with 1450 parts of water and 140 parts of concentrated hydrochloric acid. 500 parts of ice is added and then 36 parts of 23% sodium nitrite solution at 0° to 5°C within half an hour and the whole is stirred for another two hours. The diazo solution is allowed to flow through a filter into a solution of 84 parts of 1,4-dimethyl-2-hydroxy-3-cyanopyridone-(6) in 1500 parts of water, 42 parts of sodium carbonate and 1000 parts of ice. The temperature of the reaction mixture should be 4° to 8°C during the coupling; the pH is 7 to 8.

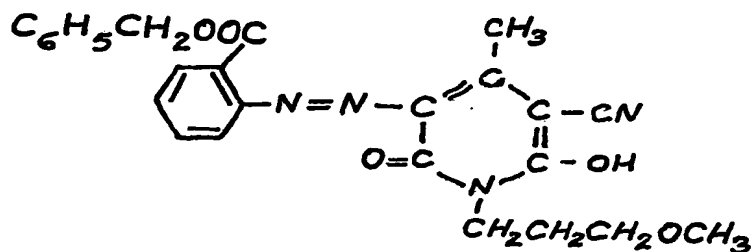
The whole is stirred overnight and the dye is then suction filtered, washed and dried. 210 parts of the dye having the formula:



is obtained.

EXAMPLE 57.

30 parts by volume of 23% aqueous sodium nitrite solution is allowed to flow slowly at 3° to 8°C into a solution of 22.7 parts of 2-amino-benzoic acid benzyl ester in 300 parts by volume of glacial acetic acid and 25 parts by volume of concentrated hydrochloric acid. During the addition of the sodium nitrite solution, a small amount of ice is added. The solution is freed from excess nitrous acid by adding sulfamic acid, and is allowed to flow slowly into a solution of 33.3 parts of N-γ-methoxypropyl-2-hydroxy-3-cyano-4-methylpyridone-(6), 5 parts of sodium hydroxide and 10 parts of sodium carbonate in 300 parts by volume of water, a pH of 7 to 8 and a temperature of 0° to 5°C being maintained by simultaneous addition of 0° to 5°C being maintained by simultaneous addition of 50% caustic soda solution and 1000 parts of ice. The whole is stirred overnight. The coupling product is suction filtered, washed with water and dried. The dye having the formula:

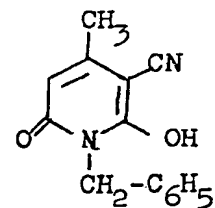
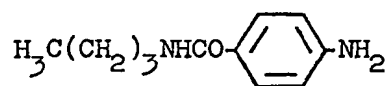


is obtained as a yellow powder which dissolves in dimethylformamide with a yellow brown color and gives greenish yellow dyeings having very good fastness properties on polyester fibers.

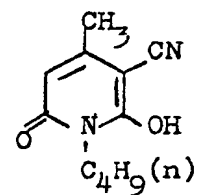
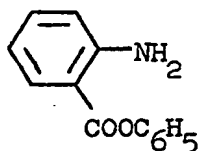
Other dyes having similar properties are obtained by using the compounds set out in the following Table. In each case the shade of the dyeing on polyesters is greenish yellow.

Example	Diazo component	Coupling component
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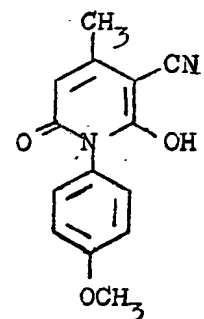
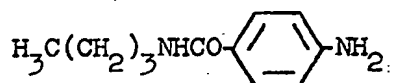
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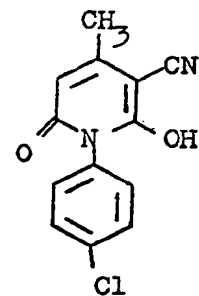
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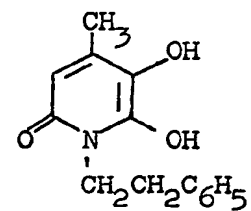
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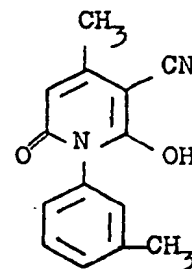
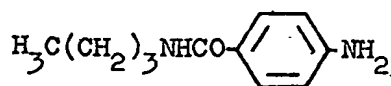
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Example	Diazo component	Coupling component
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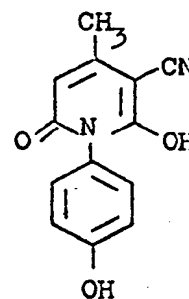
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EXAMPLE 65.

100 parts of polyethylene terephthalate cloth is treated for ninety minutes at a temperature of 100°C in a dye liquor consisting of 3000 parts of water, 9 parts of finely divided o-phenylphenol and 0.3 part of the dye from Example 56. The greenish yellow dyed cloth is then washed with water, then given a reductive purification in a liquor consisting of 3000 parts of water, 3 parts of sodium dithionite and 3 parts of 32% caustic soda solution for fifteen minutes at 35°C, washed again with water and dried.

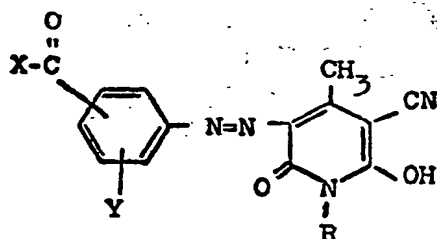
EXAMPLE 66.

100 parts of a secondary cellulose acetate is dyed for sixty minutes at 80°C in a liquor consisting of 3000 parts of water, 1.5 parts of the dye from Example 12 and 3 parts of the reaction product of 1 mole of castor oil and 40 moles of ethylene oxide. The greenish yellow dyeing obtained has outstanding light fastness and good fastness to washing.

Having regard to the provisions of Section 9 of the Patents Act, attention is directed to our copending application No. 15625/70 (Serial No 1282384).

WHAT WE CLAIM IS:—

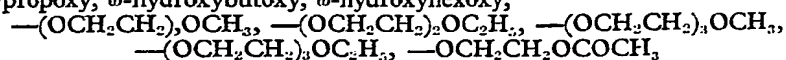
1. An azo dye having the general formula (I):



(I)

wherein, for X and Y, either

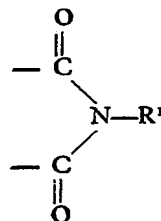
X denotes hexoxy, ethylhexoxy, benzyloxy, phenoxy, β -hydroxypropoxy, γ -hydroxypropoxy, ω -hydroxybutoxy, ω -hydroxyhexoxy,



or radical of the formula $-NHR^3$, where R^3 denotes an alkyl radical having 4 to 8 carbon atoms and optionally substituted by hydroxy or by alkoxy having 1 to 4 carbon atoms, a methoxypropyl or ethoxypropyl radical or a 5-membered to 8-membered cycloalkyl radical, and

Y denotes hydrogen, chlorine, bromine, nitro, cyano or a radical having the formula $-COX$, or

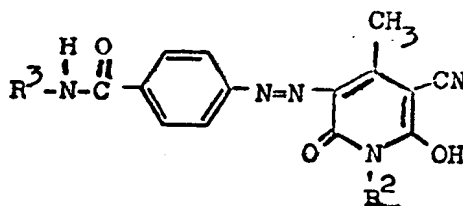
Y together with the radical $-COX$ denotes a radical which is attached to adjacent carbon atoms of the benzene ring and which has the formula



R^1 denoting hydrogen, alkyl which has 1 to 8 carbon atoms and is optionally hydroxy-, methoxy, or ethoxy-substituted, phenyl or tolyl; and

R denotes alkyl having one to four carbon atoms, alkyl having two or four carbon atoms and substituted by hydroxy, by dimethylamino or by alkoxy of one to four carbon atoms, benzyl, phenylethyl, phenyl, tolyl, 2-methoxyphenyl, 3-methoxyphenyl, 4-methoxyphenyl, 2-chlorophenyl, 3-chlorophenyl, 4-chlorophenyl, 2-hydroxyphenyl, 3-hydroxyphenyl or 4-hydroxyphenyl.

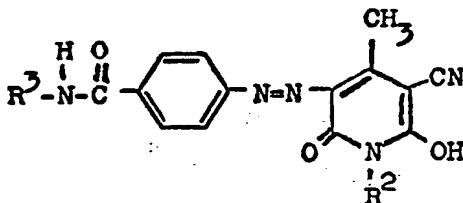
2. An azo dye having the general formula:



wherein R^2 denotes alkyl having one to four carbon atoms, or ethyl or propyl substituted by any of hydroxy, methoxy, ethoxy, propoxy and butoxy; and

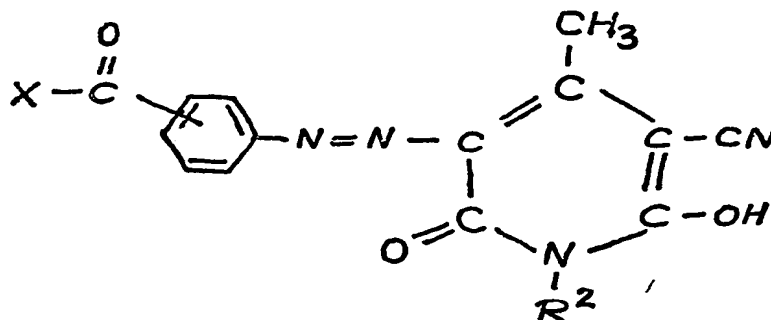
R^3 denotes alkyl having four to eight carbon atoms and optionally substituted by hydroxy or by alkoxy having one to four carbon atoms, methoxypropyl, ethoxypropyl or a five-membered to eight membered cycloalkyl radical.

3. An azo dye having the general formula:



wherein R^2 denotes methyl, or alkyl having two to four carbon atoms and optionally substituted by $-OH$, by $-OCH_3$ or by $-OC_2H_5$, and R^3 denotes butyl, cyclohexyl, β -ethylhexyl, γ -methoxypropyl, γ -ethoxypropyl, β -hydroxyethyl, β -methoxyethyl, β -hydroxypropyl or γ -hydroxypropyl.

4. An azo dye having the general formula:

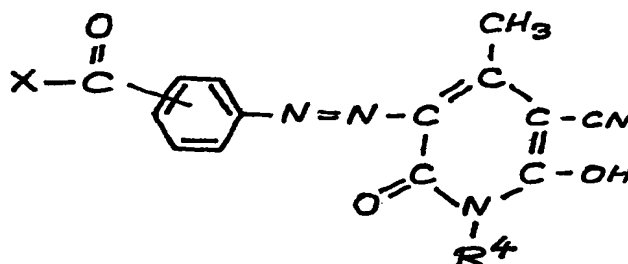


wherein R^2 has the meaning given in claim 3; and X is $-(OCH_2CH_2)_nOZ$, Z being $-CH_3$ or $-C_2H_5$, and n being 2 or 3.

5

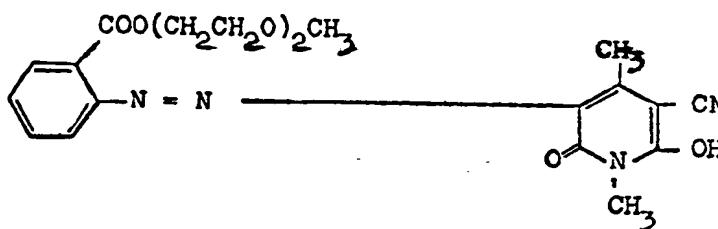
5. An azo dye having the general formula:

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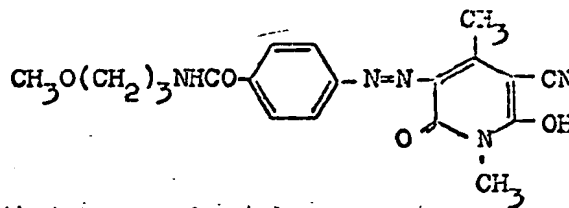


wherein X denotes $-(OCH_2CH_2)_nOCH_3$, n being 2 or 3; and R^4 denotes alkyl of one to four carbon atoms or γ -methoxy-propyl.

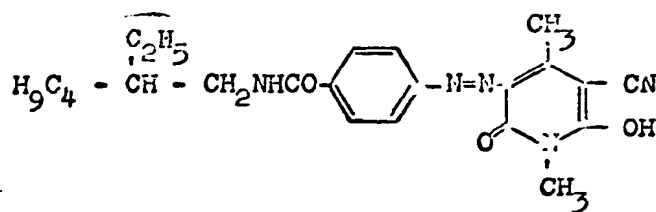
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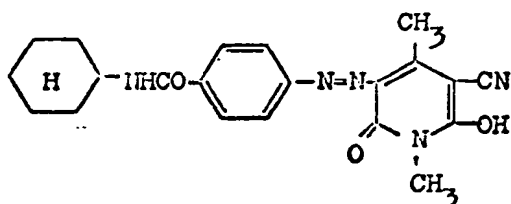
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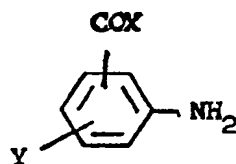


10. An azo dye as claimed in claim 1 and substantially as described in any of the foregoing Examples.

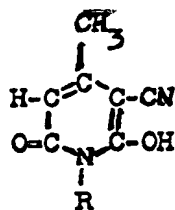
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11. A process for the production of a dye as claimed in claim 1 wherein a diazo compound of an amine having the general formula:

5



is reacted with a coupling component having the general formula:



10

where X, Y and R have the meanings given in claim 1.

10

12. A process as claimed in claim 4 carried out substantially as described in any of the foregoing Examples.

13. A dye when obtained by the process claimed in claim 11 or 12.

15

14. A process for dyeing cellulose ester and polyester textile material wherein a dye as claimed in any of claims 1 to 10 or 13 is used.

15

15. Cellulose ester and polyester textile material which has been dyed in accordance with the process of claim 14.

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